2. OVERVIEW OF EXPOSURE TO 1,3-BUTADIENE

The purpose of this chapter is to present an overview of how human exposure to 1,3-butadiene occurs. The chapter summarizes physical/chemical properties, production/use, sources/emissions, and ambient air data. Pathways of exposure are briefly described, but no quantitative estimates of exposure levels and numbers of people exposed are presented.

2.1. PHYSICAL/CHEMICAL PROPERTIES

1,3-Butadiene ($CH_2=CH-CH=CH_2$, CAS No. 106-99-0) is a colorless gas with mildly aromatic odor (Sax and Lewis, 1987). It is a noncorrosive gas and has a molecular weight of 54.09. Its boiling point is $-4.4°C$ (Weast, 1989) and its vapor pressure is 1,790 mm Hg (239 kPa) at 20°C (Santodonato, 1985). It is easily liquefied with a density of 0.6211 g/ml at 20°C/liquefied (Kirshenbaum, 1978; Verschueren, 1983). It is soluble in ethanol, diethyl ether, and organic solvents (Verschueren, 1983; Sax and Lewis, 1987; Budavari, 1989) and is also very slightly soluble in water with a solubility of 735 mg/l at 20°C. 1,3-Butadiene has a flash point of $-76°C$ (Sax and Lewis, 1987) and is slowly dimerized to 4-vinyl-1-cyclohexene (U.S. Occupational Safety and Health Administration, 1990) and may form peroxide upon exposure to air (Kirshenbaum, 1978). Since 1,3-butadiene is a highly volatile gas, it is expected to partition predominantly to the atmosphere and then undergo rapid destruction by photoinitiated reactions. The reaction with photochemically produced hydroxyl radicals has a calculated half-life of approximately 6 h and is expected to be the dominant pathway for atmospheric removal (U.S. Department of Health and Human Services [DHHS], 1992). Destruction of atmospheric 1,3-butadiene by the gas-phase reaction with ozone and by the nighttime reaction with nitrate radicals in urban areas is also expected to be significant (U.S. DHHS, 1992). The major photooxidation products of 1,3-butadiene are acrolein and formaldehyde (Maldotti et al. 1980).

There are limited data on the fate of 1,3-butadiene in soil or water. Based on its physical properties, rapid volatilization of 1,3-butadiene from either soil or water to atmosphere is expected to dominate over all other potential environmental processes. Studies performed with pure cultures indicate that 1,3-butadiene may be susceptible to microbial attack. Based on estimated values, 1,3-butadiene is not expected to adsorb significantly to soil or sediment, nor is it expected to bioconcentrate in fish or aquatic organisms (U.S. DHHS, 1992).

2.2. PRODUCTION AND USE

1,3-Butadiene was first produced in 1886 by the pyrolysis of petroleum hydrocarbons (Kirshenbaum, 1978). Commercial production of 1,3-butadiene started in the 1930s (Kosaric et al., 1987) and has been produced by three processes: catalytic dehydrogenation of *n*-butane and

n-butene, oxidative dehydrogenation of *n*-butene, and recovery from the C_4 coproduct (by-product) stream from the steam cracking process used to manufacture ethylene. The ethylene coproduct process accounts for approximately 95% of U.S. and 85% of worldwide production (Morrow, 1990). Approximately 12 billion pounds of this gas are produced annually worldwide and 3 billion pounds in the United States (Morrow, 1990; USITC, 1990).

1,3-Butadiene is used as an intermediate in the production of polymers, elastomers, and other chemicals. The major uses of this chemical are in the manufacture of styrene-butadiene rubber (synthetic rubber) and of thermoplastic resins. In 1990, 1,3-butadiene was used in the United States for styrene-butadiene rubber (30%), polybutadiene rubber (20%), adiponitrile/ hexamethylenediamine (15%), styrene-butadiene latex (10%), neoprene rubber (5%), acrylonitrile-butadiene-styrene resins (5%), exports (4%), nitrile rubber (3%), and other (including specialty polymers) (8%) (Anon., 1991).

2.2.1. Styrene-Butadiene Latex and Rubber Production

Styrene-butadiene (SB) latex and rubber production is the major use for butadiene, accounting for 40% of butadiene consumption. SB latex and rubber are used for a variety of products, including automobile tires, textiles, paper, and adhesives.

The 1994 EPA report Locating and Estimating Air Emissions From Sources of 1,3-Butadiene lists SB latex and rubber production as the major contributor to industrial butadiene emissions (EPA, 1994a). About 74% of the industrial emissions are from SB latex and rubber production. There are at least 26 facilities in the United States that produce SB latex and rubber (SRI International, 1993).

As stated previously, butadiene has a very low water solubility and high vapor pressure; thus, if it were released to an aqueous waste stream, it would immediately evaporate. It is then logical to assume, and the data confirms that, the amount of butadiene found in secondary sources such as waste water and solid waste is minimal or nonexistent. The majority of the butadiene releases during industrial production occurs via process vents, so only emission factors for process vents will be presented. The emission factors, as presented in the 1994 EPA report for process vent butadiene released during SB latex and rubber production, range from 0.00024 to 94.34 lb butadiene emitted/ton produced (mean of 7.10) measured at 18 facilities (EPA, 1994a).

2.2.2. Polybutadiene Production

The second largest use for butadiene is in the production of polybutadiene, accounting for over 20% of butadiene consumption. Polybutadiene is used in tire manufacturing and in the high-impact resin industry. Four companies at five locations in the United States currently produce polybutadiene. The estimate for process vent butadiene emissions from polybutadiene production, as stated in the 1994 EPA report, ranges from 0.00008 to 36.06 lb butadiene emitted/ton produced (mean of 6.14) measured at six facilities (EPA, 1994a).

2.2.3. Neoprene Rubber Production

Neoprene, or polychloroprene, rubber production accounts for 5% of butadiene consumption. Neoprene rubber is primarily used in the automotive industry as belts, cables, hoses, and wires. Three facilities currently produce neoprene, though only two use butadiene as a raw material and the other starts with chloroprene. The two facilities identified in the 1994 EPA report that used butadiene as a raw material yield estimated process vent butadiene emissions from neoprene production ranging from 0.32 to 6.78 lb butadiene emitted/ton produced (mean of 4.04) (EPA, 1994a).

2.2.4. Acrylonitrile-Butadiene (ABS) Resin Production

ABS resins are used to make plastic components such as automotive parts, pipes and fittings, appliances, telephones, and business machines, among many other uses. ABS production accounts for 5% of butadiene consumption. Currently, there are 10 facilities that produce ABS resin, only 6 of which use butadiene as a raw material. The estimate for process vent butadiene emissions from ABS resin production ranges from 0.16 to 10.66 lb butadiene emitted/ton produced (mean of 4.22) measured at three facilities (EPA, 1994a).

2.2.5. Nitrile Elastomer Production

Nitrile elastomer or nitrile-butyl rubber is a specialty elastomer known for its oil-, solvent-, and chemical-resistant properties. Some uses include hoses, belting, and cable manufacturing and seals and gaskets. Nitrile elastomer is produced at nine facilities in the United States and accounts for about 5% of total butadiene consumption. The estimate for process vent butadiene emissions from nitrile elastomer production ranges from 0.0004 to 17.80 lb butadiene emitted/ton produced measured at six facilities identified in the 1994 EPA report (EPA, 1994a).

2.2.6. Adiponitrile Production

Adiponitrile (hexanedinitrile) is primarily an intermediate used in the production of nylon 6,6. Three facilities produce adiponitrile, but only two of these facilities use butadiene in production. This accounts for 12% of butadiene consumption. Despite the large usage of butadiene in adiponitrile production, emissions appear to be fairly small. The estimate for process vent butadiene emissions from adiponitrile production, based on actual emissions reported at two facilities, is 0.12 lb butadiene emitted/ton produced (EPA, 1994a).

2.3. SOURCES AND EMISSION

1,3-Butadiene may be released to the environment as an intentional or fugitive emission during its production, use, storage, transport, or disposal. Its sources and emission to the environment can be classified as industrial production and use (1.6%), mobile sources (78.8%), and other miscellaneous combustion sources (19.6%) (EPA, 1994a).

Industrial butadiene emissions arise from process vents, equipment leaks, and secondary sources such as waste water treatment. Since butadiene released to aqueous systems or entering treatment plants is likely to evaporate completely, all emissions of butadiene can be considered air emissions. Actual reported emissions of butadiene are available through the Toxic Release Inventory, and the relative contribution of butadiene production to the national butadiene emissions is 0.2% (EPA, 1994a).

2.3.1. Mobile Sources

Butadiene is formed as a product of incomplete combustion of fossil fuels and has been reported in the emissions from gasoline and diesel vehicles, as well as aircraft. Emissions of butadiene from combustion sources are commonly represented as a weight percent of total organic gas emissions. The relative contribution of mobile sources to the national butadiene emissions is 78.8%, which includes both on-road and nonroad engines. Levels of butadiene in gasoline and diesel fuel are expected to be insignificant since butadiene tends to form a varnish that can be harmful to engines; therefore, refiners try to minimize the butadiene content. Since butadiene is not a component of gasoline, it is not present in mobile source evaporative or refueling emissions and will be found only in exhaust emissions (EPA, 1992).

It should be noted that a recent reevaluation by Nordlinder et al. (1996) of the Concawe report (1987) found that the concentrations of 1,3-butadiene in gasoline vapors were much lower than had been reported. Two analyses by Lofgren et al. (1991) and Ramnas et al. (1994) also found negligible amounts of 1,3-butadiene in gasoline vapors. When they compared the concentrations of benzene and butadiene in gasoline, they found concentrations to be 3%-5%

and <0.0005%, respectively. Based on these three reports, Nordlinder et al. (1996) concluded that there is no significant amount of 1,3-butadiene present in gasoline vapors.

2.3.1.1. On-Road Mobile Sources

On-road mobile sources include the following classes of vehicles: light-duty gasoline vehicles (LDGV), light-duty gasoline trucks, heavy-duty gasoline trucks, light-duty diesel vehicles, light-duty diesel trucks, heavy-duty diesel trucks, and motorcycles. On-road mobile sources account for 37.7% national butadiene emissions.

Although data on the butadiene content of motor vehicle exhaust were lacking until the late 1980s, butadiene emissions from LDGV's are now reasonably well understood. As mentioned previously, butadiene is not a component of gasoline and is not present in evaporative or refueling emissions; thus, only exhaust butadiene emissions are included. Butadiene has been found to be removed effectively from motor vehicle exhaust by catalytic convertors (McCabe et al., 1992). Thus, nearly all on-road motor vehicle butadiene emissions come from older, noncatalyst vehicles, new vehicles with nonfunctional catalysts, the cold-start emissions from catalyst vehicles, and diesel vehicles.

The emission factors calculated for all of the vehicles listed above range from 0.01 to 0.09 gm/mile (EPA, 1994b). A composite emission factor of 0.0156 gm/mile has been calculated for the calendar year 1990 by the Office of Mobile Sources (OMS) using the MOBILE model. The composite emission factor represents all vehicles classes and is based on the percentage of total vehicle miles traveled (VMT) attributable to each vehicle class (EPA, 1993a).

2.3.1.2. Nonroad Mobile Sources

Nonroad mobile sources include mobile gasoline- and diesel-powered equipment and vehicles and other equipment types. Types of equipment included in this category range from construction, industrial, and agricultural equipment to small engines used in lawnmowers, chain saws, and other gasoline-powered equipment. Nonroad vehicles include motorcycles, snowmobiles, golf carts, and all-terrain vehicles (ATVs) used for off-road recreation and recreational and commercial marine vessels. However, trains and aircraft are not generally included in the nonroad vehicle category.

Generally, most nonroad engines are in use for many years and are noncatalyst engines. The lack of a catalyst, in conjunction with the engine deterioration associated with increased equipment age, may have profound effects on the amount of butadiene emitted. The emission factors expected for the three major engines types in this categoryCgasoline-powered two-stroke

engines, gasoline-powered four-stroke engines, and diesel enginesCare generally higher (by a minimum of a factor of 10) than the gasoline engines (EPA, 1991). The EPA 1994 draft denotes that nonroad engines are expected to contribute 41% to the national butadiene emissions (EPA, 1994a).

2.3.1.3. Aircraft

Human exposure to aircraft emissions is considered to be limited to the emissions that occur during aircraft landing and take-off (LTO). Airborne aircraft are assumed to fly at sufficiently high altitudes that their emissions do not reach the surface. This assumption is likely to be valid for butadiene because of its short atmospheric lifetime.

Butadiene has been reported in aircraft LTO emissions from military, commercial, and general aviation. Based on the EPA SPECIATE database, the butadiene weight percents for aircraft LTO hydrocarbon emissions range from 1.57% for general aviation (piston engines) to 1.89% from military aircraft (jet and piston engines). The 1994 EPA report estimates that 0.1% of the national butadiene emissions is attributable to aircraft LTO (EPA, 1994a).

2.3.2. Miscellaneous Sources

This section contains an overview of the miscellaneous sources of butadiene emissions. These sources have been grouped as miscellaneous chemical production, secondary lead smelters, petroleum refining, and combustion sources (especially biomass burning). Emissions from these sources can account for 19.6% of the national butadiene emissions.

2.3.2.1. *Miscellaneous Chemical Production*

The 1994 EPA report notes that butadiene is used to produce other elastomers and plastics not mentioned previously, as well as pesticides and fungicides at 19 separate facilities in the United States (EPA, 1994a). This process accounts for 8% of the butadiene use, but only contributes 0.1% to the national average butadiene emissions. The emission factors for process vent butadiene released during miscellaneous chemical production range from 0.03 to 440 lb butadiene emitted/ton produced (product varies) measured at only four facilities.

2.3.2.2. *Secondary Lead Smelters*

Secondary lead smelting involves the reclamation of scrap automobile batteries to produce elemental and lead alloys. There are 23 such facilities in the United States, most of which are located near large population centers. The plastic and rubber components of the battery are the source of the butadiene emissions, contributing 0.4% of the national butadiene

emissions. The 1994 EPA report lists uncontrolled butadiene emissions measured from a blast furnace yielding an average emission factor of 0.79 lb/ton (EPA, 1994a).

2.3.2.3. *Petroleum Refining*

The 1992 Toxic Release Inventory contains the emission factor of 437,590 lb/year for petroleum refining. Using this emission factor would make this source the fifth largest emitter of butadiene, contributing 0.3% to the national butadiene emissions. Data are currently being collected to determine the actual contribution of petroleum refining to butadiene emissions.

2.3.3. *Combustion Sources*

Butadiene is, as mentioned previously, a product of incomplete combustion and has been reported in the emissions from gasoline and diesel vehicles, as well as aircraft. Butadiene is also released during the combustion of tobacco, biomass, and automobile tires, although only the latter two will be discussed in this section due to the scarcity of data.

2.3.3.1. *Tire Burning*

There are approximately 240 million tires discarded annually, of which only 25% are recycled. The remaining tires are discarded in landfills, stockpiles, or illegal dumps (Lemieux and DeMarini, 1992). Tires are combusted through accidental fires at stockpiles, illegal burning, tire-to-energy facilities, cement kilns, tire manufacturing facilities, and as a supplemental fuel in boilers. Butadiene is a major constituent of the tire manufacturing process and therefore it is present in emissions from tire burning. Emission factors have been calculated for the open burning of tires (EPA, 1992; Lemieux and DeMarini, 1992). These emission factors range from 234.28 lb/1,000 tons of chunk tires to 277.95 lb/1,000 tons of shredded tires. No emission factor for butadiene from tire incineration has been located.

2.3.3.2. *Biomass Burning*

Biomass burning includes residential wood combustion in both fireplaces and wood stoves, open burning such as the backyard burning of yard waste, slash burning, land clearing/burning, agricultural burning, forest fires/prescribed burning, structural fires, and other wildfires. Although these fires differ in many important characteristics, the fuels in all cases are primarily composed of wood. The relative contribution of biomass burning to the overall national butadiene emissions was calculated at 18.8% in the 1994 EPA report (EPA, 1994a).

Emission factor models based on field and laboratory data were developed by the U.S. Forest Service (Peterson and Ward, 1989). These models incorporate variables such as fuel type and combustion types (flaming or smoldering) and these models correlated butadiene emissions

with CO emissions to develop emission factors for biomass burning (Campbell and Mangino, 1994). The calculated emission factors range from 0.40 lb/ton of yard waste burned to 0.90 lb/ton for large wood burning in forest fires and prescribed burning.

Butadiene emissions have been reported from the combustion of wood (Sandberg et al., 1975; Ward and Hao, 1992). The data of Ward and Hao (1992), in which both butadiene and benzene were quantified from biomass burning, provides a butadiene:benzene ratio of 0.36 for wood smoke.

2.4. AMBIENT CONCENTRATION OF 1,3-BUTADIENE

2.4.1. Air

In 1989, total emissions of 1,3-butadiene to the air in the United States were estimated at approximately 2,512 tonnes from 158 locations; total land releases were estimated at 6.7 tonnes (U.S. National Library of Medicine, 1991).

2.4.1.1. *Ambient Monitoring Data*

Several EPA databases exist that contain the results of various air toxics monitoring programs. These programs have set up monitoring devices that are used to collect air samples all over the United States over a period of months or years. Three of these programs/databases contain data on 1,3-butadiene. This section summarizes the three monitoring programs and presents annual average concentrations of 1,3-butadiene derived from these programs.

One of these programs is the Aerometric Information Retrieval System (AIRS), which became operational in 1987 and uses a network of monitoring stations called the State and Local Air Monitoring System (SLAMS) (EPA, 1989a). This network consists of monitoring stations set up by every State in accordance with regulations promulgated in response to requirements of the Clean Air Act. EPA's Office of Air Quality Planning and Standards (OAQPS) administers the AIRS program.

The AIRS program allows State and local agencies to submit local air pollution data and also have access to national air pollution data (EPA, 1989a). EPA uses data from AIRS in order to monitor the States' progress in attaining air quality standards for ozone, carbon monoxide, nitrogen oxides, sulfur oxides, and lead through the use of State Implementation Plans (SIPS). In addition to containing information about each monitoring site, including the geographic location of the site and who operates it, the AIRS program also contains extensive information on the ambient levels of many toxic compounds. The AIRS database catalogs ambient air pollution data from 18 to 55 monitors in 15 to 23 urban areas, depending on the pollutant. These monitors collect a 24-h sample every 12 days. However, in some cases not every target

compound was detected in every sample. Where this occurred, half the minimum detection limit was used in the averaging of the data for this summary. The annual average ppb for each site was calculated using only those sites that provided four quarters of monitoring data. The cities monitored and the average concentrations determined can be found in Table 2-1.

Another air monitoring program is the Urban Air Toxic Monitoring Program (UATMP), which the EPA developed in 1987 to assist State and local agencies in determining the nature and extent of urban air toxic pollution (McAlister et al., 1989, 1990, 1991; Wijnberg and Faoro, 1989). Data from the UATMP also is used in air toxic risk assessment models (EPA 1989b, c; EPA 1990a, b). In 1989, the UATMP had 14 monitors in 12 urban areas, and in 1990, the UATMP had 12 monitors in 11 urban areas, of which 9 also participated in the 1989 monitoring program.

In 1989 and 1990, the UATMP network simultaneously monitored 37 nonmethane organic compounds, selected metals, benzo(a)pyrene (1989 only), formaldehyde, acetaldehyde, and acetone for a 24-h period once every 12 days. The UATMP database lists the data collected from the monitoring network using two methods. In the first method, only the concentrations above the detection limit of the compound are included in the data. In the second method, if the concentration of a compound is below the detection limit, then one-half of the compound's detection limit is incorporated into the data. The second method was used because it seemed more reasonable and allowed a greater number of samples to be averaged. Data collected in 1989 and 1990 were used in this summary. The cities monitored and the average concentrations determined can be found in Table 2-2.

The monitoring data for the UATMP that were collected from 1991 to 1994 have not yet been released as separate reports. The data collected in those 4 years were entered into and reported as part of the 1991-1994 AIRS database.

The National Ambient Volatile Organic Compounds (NAVOC) Database contains approximately 175,000 records on the concentrations of 320 volatile organic compounds (VOCs) observed in 1-h air samples taken every 24 h between 1970 and 1987 (Shah and Heyerdahl, 1988; Hunt et al., 1988). However, only the most current NAVOC data, taken during 1987, is used in this summary. In addition, samples that had nondetects of 1,3-butadiene were included as one-half the detection limit in averaging the data for this summary. The NAVOC Database includes air samples collected using indoor and outdoor monitoring devices. Personal monitors were also used. The types of locations of outdoor monitoring sites included remote, rural, suburban, and urban areas, as well as near specific point sources of VOCs. Indoor monitoring

Table 2-1A. Summary of 1,3-butadiene ambient data from the EPA Aerometric Information Retrieval System (AIRS) for 1988 to 1991

Average concentration (ppb)				Sampling sites	Land use of monitor location	Number of samples			
1988	1989	1990	1991			1988	1989	1990	1991
	0.13			Washington, DC	Commercial/Urban & Center City		7		
	0.29			Ft. Lauderdale, FL	Commercial/Urban & Center City		29		
	0.14			Miami, FL	Commercial/Urban & Center City		31		
	0.19			Miami, FL	Commercial/Urban & Center City		6		
	0.14			Miami, FL	Commercial/Urban & Center City		6		
	0.13			Miami, FL	Commercial/Urban & Center City		6		
	0.10			Chicago, IL	Commercial/Urban & Center City		10		
	0.29			Chicago, IL	Residential/Suburban		25		
	0.73			Chicago, IL	Mobile/Urban & Center City		9		
	0.22			St. Clair Co., IL	Industrial/Suburban		29		
	0.31			St. Clair Co., IL	Industrial/Suburban		4		
	0.30			St. Clair Co., IL	Industrial/Suburban		4		
	0.25			St. Clair Co., IL	Industrial/Suburban		4		
	0.13			Wichita, KS	Residential/Suburban		29		
	0.16			Wichita, KS	Residential/Urban & Center City		8		
0.44				Louisville, KY	Commercial/Urban & Center City	6			
	0.43			Baton Rouge, LA	Commercial/Urban & Center City		29		
	0.41			Baton Rouge, LA	Commercial/Urban & Center City		4		
	0.53			Baton Rouge, LA	Commercial/Urban & Center City		4		

Table 2-1A. Summary of 1,3-butadiene ambient data from the EPA Aerometric Information Retrieval System (AIRS) for 1988 to 1991 (continued)

Average concentration (ppb)				Sampling sites	Land use of monitor location	Number of samples			
1988	1989	1990	1991			1988	1989	1990	1991
	0.37			Baton Rouge, LA	Commercial/Urban & Center City		4		
		0.33	0.07	Detroit, MI	Commercial/Urban & Center City			19	28
	0.12			St. Louis, MO	Commercial/Urban & Center City		28		
	0.23			Camden, NJ	Residential/Suburban		29		
	0.16			Camden, NJ	Residential/Suburban		4		
	0.18			Camden, NJ	Residential/Suburban		4		
	0.15			Camden, NJ	Residential/Suburban		4		
	0.26			Newark, NJ	Industrial/Urban & Center City		9		
	0.20			Plainfield, NJ	Residential/Suburban		9		
	0.25			New York, NY	Residential/Urban & Center City		9		
	0.29			New York, NY	Commercial/Urban & Center City		9		
	0.11			Dallas, TX	Commercial/Urban & Center City		23		
1.11	0.60	0.72		Houston, TX	Residential/Suburban	6	30	4	
0.47				Burlington, VT	Commercial/Urban & Center City	6			
		0.20	0.11	Arlington Co., VA	Commercial/Urban & Center City			13	18
		0.16	0.12	Henrico Co., VA	Residential/Suburban			21	12
		0.22	0.11	Hampton, VA	Residential/Suburban			14	22
		0.13	0.06	Hopewell, VA	Residential/Suburban			16	15
		0.24	0.12	Roanoke, VA	Residential/Suburban			14	22
0.67 ppb	0.26 ppb	0.29 ppb	0.10 ppb						

1,3-Butadiene Average Concentration Across Sites by Year

Table 2-1B. Summary of 1,3-butadiene ambient data from the EPA Aerometric Information Retrieval System (AIRS) for 1992 to 1994

Average concentration (ppb)			Sampling sites	Land use of monitor location	Number of samples		
1992	1993	1994			1992	1993	1994
	0.12	0.33	Jefferson Co., AL	Residential/Rural		83	79
		0.19	Jefferson Co., AL	Residential/Rural			9
	4.32	0.78	Tarrant City, AL	Residential/Suburban		82	81
		0.91	Tarrant City, AL	Residential/Suburban			10
	0.07	0.15	Shelby Co., AL	Agricultural/Rural		50	78
	0.30	0.30	Fresno, CA	Residential/Suburban		30	31
		0.54	Clovis, CA	Residential/Urban & Center City			111
	0.28	0.27	Bakersfield, CA	Residential/Urban & Center City		30	9
		0.35	Bakersfield, CA	Commercial/Urban & Center City			23
		0.63	Bakersfield, CA	Commercial/Urban & Center City			105
	0.65	0.53	Los Angeles, CA	Residential/Urban & Center City		26	30
	0.16	0.15	Roseville, CA	Mobile/Suburban		23	31
	0.41		Citris Heights, CA	Residential/Suburban		6	
		0.53	Sacramento, CA	Residential/Suburban			84
	0.34	0.27	El Cajon, CA	Commercial/Suburban		28	28
	0.18	0.17	Simi Valley, CA	Residential/Suburban		28	29
	0.36	0.28	Washington, DC	Commercial/Urban & Center City		10	16
	0.32	0.46	Washington, DC	Commercial/Urban & Center City		13	15
	0.09	0.18	Chicago, IL	Industrial/Urban & Center City		6	14

Table 2-1B. Summary of 1,3-butadiene ambient data from the EPA Aerometric Information Retrieval System (AIRS) for 1992 to 1994 (continued)

Average concentration (ppb)			Sampling sites	Land use of monitor location	Number of samples		
1992	1993	1994			1992	1993	1994
	0.06	0.08	Lemont, IL	Residential/Suburban		15	13
	0.10	0.11	St. Clair Co., IL	St. Louis Metro Area		10	12
	0.17	0.26	Kansas City, KS	Industrial/Urban & Center City		11	13
	0.42	0.43	Baton Rouge, LA	Commercial/Urban & Center City		14	8
	0.15	0.22	Glen Burnie, MD	Commercial/Suburban		60	54
	0.25	0.26	Essex, MD	Residential/Suburban		39	58
0.18	0.17		Baltimore, MD	Residential/Suburban	56	59	
0.09			Baltimore, MD	Industrial/Suburban	21		
0.10	0.12		Baltimore, MD	Industrial/Urban & Center City	50	50	
0.26	0.25	0.28	Baltimore, MD	Residential/Urban & Center City	58	57	48
0.09	0.10		Baltimore, MD	Industrial/Urban & Center City	39	48	
0.45	0.05		Alma, MI	Commercial/Rural	22	14	
0.06	0.08		Portage, MI	Industrial/Suburban	25	4	
0.08	0.09	0.07	Midland, MI	Commercial/Rural	56	61	60
0.07	0.07	0.07	Midland, MI	Commercial/Rural	55	61	22
0.07	0.07	0.07	Midland, MI	Industrial/Rural	55	61	61
0.07	0.07	0.07	Midland, MI	Agricultural/Rural	55	61	61
0.07	0.08	0.07	Midland, MI	Industrial/Rural	55	60	61
0.07	0.07	0.07	Midland, MI	Residential/Suburban	28	31	11
0.07	0.07	0.07	Midland, MI	Residential/Rural	28	30	11
0.72	0.08		Detroit, MI	Commercial/Urban & Center City	24	15	

Table 2-1B. Summary of 1,3-butadiene ambient data from the EPA Aerometric Information Retrieval System (AIRS) for 1992 to 1994 (continued)

Average concentration (ppb)			Sampling sites	Land use of monitor location	Number of samples		
1992	1993	1994			1992	1993	1994
	0.26	0.49	Camden, NJ	Residential/Suburban		14	13
	0.63	0.73	Newark, NJ	Industrial/Urban & Center City		8	9
	0.72	0.79	Plainfield, NJ	Residential/Suburban		8	8
		0.70	Nassau Co., NY	Commercial/Suburban			9
	0.19		Philadelphia, PA	Residential/Suburban		38	
		0.08	San Antonio, TX	Residential/Suburban			21
	0.24	0.37	Clute, TX	Residential/Suburban		29	53
	0.18	0.21	Brownsville, TX	Commercial/Urban & Center City		7	15
	0.29	0.37	Brownsville, TX	Commercial/Urban & Center City		19	59
	0.32		Dallas, TX	Commercial/Urban & Center City		82	
	0.20	0.37	Dallas, TX	Industrial/Rural		34	58
	0.41	1.68	Odessa, TX	Residential/Suburban		39	59
	0.18	0.37	Midlothian, TX	Agricultural/Rural		39	51
	0.45	0.43	El Paso, TX	Commercial/Urban & Center City		14	15
	0.98	1.16	El Paso, TX	Commercial/Urban & Center City		79	79
		1.49	El Paso, TX	Commercial/Urban & Center City			9
	0.83	1.29	El Paso, TX	Commercial/Suburban		8	4
	0.21	0.38	El Paso, TX	Residential/Suburban		22	58
0.29	0.22	1.54	Texas City, TX	Residential/Urban & Center City	5	35	51
	0.35	0.29	Texas City, TX	Residential/Suburban		12	15
0.19	0.30	0.56	Harris Co., TX	Agricultural/Suburban	5	28	59

Table 2-1B. Summary of 1,3-butadiene ambient data from the EPA Aerometric Information Retrieval System (AIRS) for 1992 to 1994 (continued)

Average concentration (ppb)			Sampling sites	Land use of monitor location	Number of samples		
1992	1993	1994			1992	1993	1994
	0.44	0.81	Houston, TX	Industrial/Suburban		39	54
	0.24	0.64	Houston, TX	Industrial/Suburban		33	58
0.05	0.39	0.73	Houston, TX	Industrial/Suburban	6	37	58
	0.56		Beaumont, TX	Residential/Suburban		78	
0.05	0.25	0.37	Beaumont, TX	Residential/Suburban	7	36	59
0.10	0.23	0.44	Port Arthur, TX	Residential/Suburban	6	45	57
	0.32	0.43	Port Neches, TX	Industrial/Suburban		18	58
		5.95	Port Neches, TX	Residential/Urban & Center City			23
	5.22	6.11	Port Neches, TX	Residential/Suburban		11	14
	0.18	0.37	Corpus Christi, TX	Commercial/Suburban		39	52
		0.18	West Orange, TX	Residential/Suburban			27
		0.33	Smith Co., TX	Mobile/Rural			32
	0.20	0.57	Fort Worth, TX	Commercial/Urban & Center City		80	77
		0.80	Fort Worth, TX	Commercial/Urban & Center City			8
		0.06	Fort Worth, TX	Commercial/Suburban			9
		0.05	Grapevine, TX	Residential/Urban & Center City			15
		0.13	Austin, TX	Commercial/Urban & Center City			21
	0.31	0.49	Burlington, VT	Commercial/Urban & Center City		13	15
	0.15	0.44	Rutland, VT	Commercial/Urban & Center City		13	15
	0.08	0.09	Waterbury, VT	Commercial/Suburban		14	15
0.16 ppb	0.40 ppb	0.59 ppb					

1,3-Butadiene Average Concentration Across Sites by Year

Table 2-2. Summary of 1,3-butadiene ambient data from the Urban Air Toxics Monitoring Program (UATMP)

Average concentration (ppb)[a]		Sampling sites	Land use of monitor location	Sampling time/frequency	Detected/total	
1989	1990				1989	1990
0.39	0.36	Baton Rouge, LA	Urban/Center City-Commercial	24-Hour/Every 12 Days	11/31	8/29
0.24	0.06	Chicago, IL	Suburban-Residential	24-Hour/Every 12 Days	10/27	4/29
0.20	0.10	Camden, NJ	Suburban-Residential	24-Hour/Every 12 Days	19/32	9/30
0.08		Dallas, TX	Urban/Center City-Commercial	24-Hour/Every 12 Days	8/25	
0.20		Fort Lauderdale, FL	Urban/Center City-Commercial	24-Hour/Every 12 Days	18/31	
0.60	0.47	Houston, TX	Suburban-Residential	24-Hour/Every 12 Days	23/34	111/28
0.11		Miami, FL	Urban/Center City Commercial	24-Hour/Every 12 Days	7/33	
	0.06	Pensacola, FL	Suburban-Industrial	24-Hour/Every 12 Days		6/42
0.09		St. Louis, MO	Urban/Center City-Commercial	24-Hour/Every 12 Days	12/30	
0.20	0.06	Sauget, IL	Suburban-Industrial	24-Hour/Every 12 Days	7/31	2/27
0.11	0.10	Washington, DC-1	Urban/Center City-Commercial	24-Hour/Every 12 Days	9/27	11/30
0.29	0.15	Washington, DC-2	Urban/Center City-Commercial	24-Hour/Every 12 Days	19/27	12/27
0.16	0.06	Wichita, KS-1	Urban/Center City-/Residential	24-Hour/Every 12 Days	10/31	1/30
0.09		Wichita, KS-2	Suburban-Residential	24-Hour/Every 12 Days	7/31	
	11.09	Port Neches, TX	Suburban-Residential	24-Hour/Every 12 Days		24/28
	0.10	Orlando, FL	Urban/Center City-Commercial	24-Hour/Every 12 Days		8/28
	0.06	Toledo, OH	Suburban-Residential	24-Hour/Every 12 Days	4/21	
0.21	1.02					

1,3-Butadiene Average Concentration in ppb[b]

[a]The arithmetic average concentration of all samples using half minimum detection limit (MDL) value for samples in which the compound was not found.

[b]Calculated by averaging all 390 samples taken from 13 sites equally in 1989 and 349 samples from 12 sites in 1990.

sites consisted of nonindustrial workplaces and residential environments. Personal monitors also are included in the indoor category. This database was an interim precursor to the air toxics portion of AIRS. For this summary, only the outdoor urban data were used. The cities monitored and the average concentrations determined can be found in Table 2-3.

Table 2-4 summarizes the average concentrations (in ppb) of 1,3-butadiene found at the monitoring sites of each air monitoring program. The table also shows the total number of observations for each average and the number of sites that monitored the compounds in each program. For AIRS, the average concentrations of 1,3-butadiene are listed separately for 1987 through 1994. Some of the highest averages in the AIRS database were from suburban residential sites in Houston and Port Neches, TX. Both of these cities have high point-source emissions that could be affecting the monitor. The AIRS and UATMP data from Houston and Port Neches, TX, were excluded to create alternate annual averages (ppb and $\mu g/m^3$) for the years 1988 through 1994 (where applicable) and are presented in Table 2-4. This alternate annual average may be more representative of areas that are not near strong point sources.

Tables 2-5, 2-6, and 2-7 regroup and summarize Tables 2-2, 2-3, and 2-4 according to the sampling locations, i.e., rural, suburban, or urban settings. The data obtained from Port Neches, TX, were not included in these averages because of the elevated levels due to industrial emissions.

It should be noted that methods of averaging the data are not consistent between the air monitoring databases. Also, in the NAVOC monitoring network, samples were taken for 1 h in a 24-h period while the other monitoring networks collected a 24-h air sample every 12 days.

It should also be noted that the ambient levels detected in these three databases are not meant to be indicative of an individual's actual exposure to 1,3-butadiene. Times and concentrations in microenvironments other than the outdoors need to be taken into consideration, i.e., accounting for integrated exposure.

In addition, the ambient levels include contributions from a variety of source categories. Typically, ambient monitoring data are adjusted to represent the amount attributed to a particular source using emissions inventory apportionment. The derivation of an urban annual average exposure estimate for all mobile sources will be used for illustration purposes (EPA, 1993a). The range of ambient data from Table 2-4 (using alternate annual averages when available) is 0.22 to 1.02 $\mu g/m^3$ (0.10 to 0.46 ppb). When this range is adjusted by the estimated proportion of the inventory that is contributed by mobile sources (78.7%) and for integrated exposure to account for time spent indoors and outdoors, the range becomes 0.11 to 0.50 $\mu g/m^3$ (0.05 to 0.23 ppb).

Table 2-3. Summary of outdoor urban data from the National Ambient Volatile Organic Compounds (NAVOC) Database

Sample years	Average concentration used (ppb)	Number of samples	Sampling sites	Land use of monitor location	Number of samples/ sampling time
9/22/87 to 10/4/87	0.30	2	Bakersfield, CA	Urban	1/24-hours
9/16/87 to 9/28/87	0.35	2	Concord, CA	Urban	1/24-hours
10/4/87 to 10/4/87	0.60	1	Fremont, CA	Urban	1/24-hours
10/4/87 to 10/4/87	0.40	1	Richmond, CA	Urban	1/24-hours
9/9/87 to 10/7/87	0.25	2	San Jose, CA	Urban	1/24-hours
9/29/87 to 9/27/87	0.30	1	Stockton, CA	Urban	1/24-hours
Overall 1,3-Butadiene average concentration: 0.344 ppb[a]					

[a]Calculated by averaging all nine samples taken from six cities equally.

Table 2-4. Summary of air monitoring program results for 1,3-butadiene

	Annual average ppb ($\mu g/m^3$)	Alternate annual average[a] ppb ($\mu g/m^3$)
AIRS		
1988 level		
(ppb)	0.67(1.48)	0.46(1.02)[b]
# Obs.	18	12
# Sites	3	2
1989		
(ppb)	0.23(0.57)	0.25(0.55)[b]
# Obs.	399	369
# Sites	30	29
1990		
(ppb)	0.29(0.64)	0.21(0.46)[b]
# Obs.	101	97
# Sites	7	6
1991		
(ppb)	0.10(0.22)	----[c]
# Obs.	117	
# Sites	6	
1992		
(ppb)	0.16 (0.40)	0.16 (40)[b]
# Obs.	656	650
# Sites	20	19
1993		
(ppb)	0.40(0.88)	0.32(0.71)[d]

# Obs.	2069	1,931
# Sites	64	59
1994		
(ppb)	0.59(1.30)	0.42(0.92)[d]
# Obs.	2666	2,401
# Sites	70	64

Table 2-4. Summary of air monitoring program results for 1,3-butadiene (continued)

	Annual average ppb (µg/m³)	Alternate annual average[a] ppb (µg/m³)
UATMP		
1989		
(ppb)	0.21 (0.46)	----[e]
# Obs.	390	
# Sites	13	
1990		
(ppb)	1.02(2.25)	0.12(0.27)[b]
# Obs.	349	293
# Sites	12	10
NAVOC		
1987		
(ppb)	0.34(0.75)[f]	no data
# Obs.	9	
# Sites	6	

[a]Alternate averages do not include data from Houston and Port Neches, TX, due to impacts from strong point sources.
[b]Average ppb from all 4-quarter data sites, excluding Houston, TX.
[c]Houston, TX, was not monitored during this 4-quarter period.
[d]Average ppb from all sites, excluding Houston and Port Neches, TX.
[e]Port Neches, Texas, was not monitored during this 4-quarter period.
[f]All urban California sites.

Table 2-5. Summary of 1,3-butadiene ambient data from the EPA Aerometric Information Retrieval System (AIRS) based on sampling locations

	Rural area			Suburban area			Urban area		
Year	Range	Average[a]	Total samples/ number of locations	Range	Average	Total samples/ number of locations	Range	Average	Total samples/ number of locations
1988				---	1.11	6/1	0.44 - 0.47	0.46	12/2
1989				0.13 - 0.60	0.25	151/12	0.10 - 0.73	0.27	237/18
1990				0.16 - 0.72	0.29	95/5	0.20 - 0.33	0.27	32/2
1991				0.06 - 0.12	0.10	71/4	0.07 - 0.11	0.09	46/2
1992	0.07-0.45	0.13	271/6	0.05 - 0.19	0.10	154/7	0.09 - 0.72	0.29	176/5
1993	0.05-0.20	0.10	494/10	0.06 - 4.32	0.41	864/31	0.08 - 0.98	0.31	580/21
1994	0.07-0.37	0.18	522/11	0.06 - 1.68	0.45	1135/32	0.05 - 1.54	0.62	780/24

[a]1,3-Butadiene average concentration in ppb.

Table 2-6. Summary of 1,3-butadiene data from Table 2-2 based on sampling locations

	Suburban			Urban		
Year	Range	Average[a]	Total samples/ number of locations	Range	Average	Total samples/ number of locations
1989	0.09 - 0.60	0.27	155/5	0.08 - 0.39	0.18	235/8
1990	0.06 - 0.47	0.14	177/6	0.06 - 0.36	0.15	144/5

[a]1,3-Butadiene average concentration in ppb.
[b]The arithmetic average concentration of all samples using one-half minimum detection limit value for samples in which the compound was not found.

Table 2-7. Summary of 1,3-butadiene data from Table 2-3 based on sampling locations

	Urban		
Year	Range	Average[a]	Total samples/number of locations
1987	0.25 - 0.60	0.37	9/6

[a]1,3-Butadiene average concentration in ppb.

2.4.1.2. *Ambient Source Apportionment*

There are three studies that attempt to apportion sources as to their contribution to ambient levels of 1,3-butadiene. The studies assume that all emissions to the atmosphere contribute proportionally to ambient concentration. These three studies are summarized in Table 2-8.

As observed in Table 2-8, the source apportionment conducted by Systems Applications International for the American Automobile Manufacturers Association (Ligocki, 1993) contains the category of biomass burning as a large part of the inventory. The weight percentage of butadiene in TOG for emissions from residential wood combustion, open burning, forest fires, and other burning that are used in this analysis are derived from a single estimate provided in EPA's SPECIATE database. An actual 1,3-butadiene TOG weight percentage for incineration of wood was not found in the literature; therefore, the solid waste incineration TOG weight percentage was used. There is a great deal of uncertainty connected with the 1,3-butadiene emission estimates that were developed for the biomass burning as well as for emissions from aircraft. Many of the limitations revolve around the lack of real-world data on actual 1,3-butadiene emissions and exposures for the scenarios mentioned above, as well as the allocation of these scenarios nationwide. The emissions from residential wood combustion and forest fires vary by season and region of the country. The mobile source and stationary source emissions would, for the most part, remain constant throughout much of the year.

2.4.2. Indoor Exposure to 1,3-Butadiene

Information on 1,3-butadiene concentrations in homes or public buildings is limited at this time. Indoor concentrations of 1,3-butadiene are primarily dependent on the presence of environmental tobacco smoke (ETS) (CARB, 1992). Several studies indicate that on the average most individuals spend anywhere from about 60% to 70% (Robinson et al., 1989; EPA, 1993b) of their time each day indoors at their residence. In addition, individuals also spend a lot of time at indoor workplaces. This makes indoor air a major route of exposure to 1,3-butadiene for individuals who are exposed to tobacco smoke. It is also apparent that the potential for indoor exposure can exceed outdoor exposure if ETS is taken into consideration. Löfroth et al. (1989) and Brunnemann et al. (1990) measured 1,3-butadiene emissions in sidestream smoke ranging from 200 to 400 μg/cigarette and 1,3-butadiene levels in smoke-filled bars ranging from 2.7 to 19 μg/m^3. Further research and measurements are needed to quantify typical indoor 1,3-butadiene exposures.

Table 2-8. Summary of the relative contributions to ambient 1,3-butadiene emissions given as percent of total mg/year

Study	Mobile sources[a]	Stationary point and area sources[b]	Aircraft	Biomass burning[c]
EPA, 1994a	78.7	2.4	0.1	18.8
CARB, 1992	96[d]	4	Included under mobile sources	ND[e]
Ligocki, 1993	57	5	3	35

[a]Mobile sources included on-road and off-road vehicles and generally excluded trains and aircraft.
[b]Area and point sources generally included all manufacturing and industrial process, oil and gas production facilities, commerce, residential fuel combustion, and other stationary fuel combustion.
[c]Biomass burning includes residential wood combustion, incineration, and other biomass burning.
[d]The CARB off-road apportionment of mobile sources includes trains and aircraft.
[e]ND=not determined.

2.4.3. Water

Although 1,3-butadiene has been detected in drinking water in the United States (U.S. EPA, 1978; Kraybill, 1980), it is not clear what happens to the chemical in the body (U.S. DHHS, 1992). Total releases to ambient water in 1989 were estimated to be 65 tonnes (U.S. National Library of Medicine, 1991).

2.4.4. Food

Certain cooking oils release butadiene on heating. For example, 1,3-butadiene emissions are approximately 22-fold higher from unrefined Chinese rapeseed oil than from heated peanut oil. Of three fatty acids tested, heated linolenic acid produced the greatest amount of 1,3-butadiene. Although cooking oils in the U.S. are refined for purity, U.S. rapeseed oil (canola) also emitted 1,3-butadiene (Shields et al., 1995). Also, levels of <0.2 μg/kg 1,3-butadiene were found in retail soft margarine; the plastic tubs containing the margarine contained < 5-310 μg/kg (Startin and Gilbert, 1984).

2.5. PATHWAYS OF EXPOSURE

The 1992 U.S. DHHS report states that although 1,3-butadiene undergoes rapid destruction in the atmosphere, it is almost always present at very low concentrations in urban and suburban areas. Automobile exhaust is a constant source of 1,3-butadiene release to the atmosphere. Because of the compound's presence in the atmosphere, the general population is exposed to ppb levels of 1,3-butadiene through inhalation. Exposure to 1,3-butadiene may also

occur from the inhalation of cigarette smoke, or possibly the smoke from wood fires. Possible ingestion of contaminated drinking water may also lead to low levels of exposure, although the concentration of this compound in drinking water has not been well characterized. The levels of 1,3-butadiene in soil are not known. Elevated levels of exposure for the general population may occur for those near its site of manufacture or facilities where it is made into polymeric materials.

Occupational exposure to 1,3-butadiene is expected to be limited to those working at facilities that manufacture 1,3-butadiene or convert it into commercial polymers. Exposure by inhalation is expected to be the dominant pathway for exposure.